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### Synthesis and Properties of Poly(Styrene-co-Phosphonate-Containing Maleimide)

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## Synthesis and Properties of Poly(Styrene-co-Phosphonate-Containing Maleimide)

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### ABSTRACT

Soluble copolymers of diethyl(*p*-(*N*-phenyl)maleimide)phosphonate (4P), diphenyl (*p*-(*N*-phenyl)maleimide)phosphonate (PP), diethyl(*p*-(*N*-(2',6'-dibromophenyl)maleimide)phosphonate) (BrP) with styrene (St) were synthesized by radical polymerization in toluene at 70°C using 2,2'-azobisisobutyronitrile (AIBN) as initiator. The comonomer reactivity ratios were calculated by the conventional Fineman-Ross, Joshi-Joshi, and Kelen-Tüdös methods. The glass transition temperatures ( $T_g$ s) and thermal degradation of copolymers were determined by differential scanning calorimetric (DSC) and thermo-gravimetric analysis (TGA) methods, respectively. The introduction of phosphonate side-chain into maleimide (MI) monomers changed the comonomer reactivity ratio with St from an alternating to azeotropic copolymerization. The curves of  $T_g$ s vs. the different compositions of the above synthesized MI–St copolymers matched the modified Johnston's equation as increasing the affect of weight ratio on alternating-segment, and exhibited an S-shaped curve of deviation in comparison with the Fox's equation. As the azeotropic composition of the

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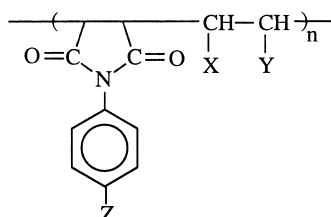


above copolymers nearby Fox's equation, their thermal stability and flame retardancy could be enhanced simultaneously by the synergy effect of their comonomers. Furthermore, a rigid structure or polar bromine atom within the phosphonate-containing MI segment of copolymer also could further promote its thermal stability and flame retardancy.

**Key Words:** Poly(styrene-co-phosphonate-containing maleimide); Reactivity ratio; Thermal stability; Flame retardancy.

## INTRODUCTION

*N*-aryl maleimide (AM) monomers, such as *N*-phenyl maleimide (PM), *N*-hydroxyphenyl maleimide (HPM), and halide-substituted *N*-hydroxy-phenyl maleimide (XHPM), were usually copolymerized with ethylene or propylene series monomers to promote their heat and fire resistance. Much research about the AM copolymers, such as the copolymers with styrene (St),<sup>[1]</sup> methyl methacrylate(MMA),<sup>[2]</sup> and acrylonitrile,<sup>[3]</sup> have been reported so far.



These copolymers synthesized by introducing the rigid and high thermal stability of AM segment possess the higher softening points (or  $T_g$ ) and good fire resistance. Comparing the double bonds of AM and St comonomers with poor-electron and rich-electron density, respectively, a close complete alternating copolymer can be formed by free radical copolymerization. The copolymerization behavior of truly alternating St-maleic anhydride copolymer has already been reported in much of the research.<sup>[4-7]</sup> However, the St-AM systems are still rarely seen in the literature.<sup>[8]</sup> On the other hand, the HPM-containing copolymer as a result of the competition and interference of HPMS hydrogen bonds also lower its copolymerization degree. Therefore, there are many reports<sup>[9,10]</sup> about the HPM monomer modified by the end-capping method to form phenoxy-substituted structure to increase its copolymerization degree. Until recently, applications of *N*-substituted maleimide (MI) polymers include photo-resist with high  $T_g$ ,<sup>[11,12]</sup> flexibilizer for thermosetting polymers,<sup>[13-16]</sup> non-linear polymer with high  $T_g$  and flame retardant,<sup>[17]</sup> etc. However, studies on the fire retardancy of these above series products, e.g., halogen-containing XHPM having both the MI's thermal stability and the halogen's fire retardancy, are still rarely seen in the literature.

The phosphorus-containing polymers can inhibit the evolution of smoke or toxic substances during decomposition process. They have better fire retardancy than a halogen-containing one. The synthesis of reactive phosphorus-containing monomers, and homopolymers or copolymers have now become the mainstream in the present research. It should be one of the most convenient ways to introduce phosphorus-containing



segments that combined a reactive phosphorus-containing monomer with the original monomer to form a flame retardant copolymer. Much research had been done on these designed monomers and their derived polymers or copolymers.<sup>[18–21]</sup> However, the introducing phosphorus groups into flame retardant materials shall lower their  $T_g$  and thermal stability, and also lessen their applied interests. Therefore, our team has already designed a series of different phosphonate-containing side chains introducing into *N*-AMs with high thermal stability, which could be polymerized by a free radical initiator to form the soluble homopolymer.<sup>[22]</sup> In this paper, we will discuss the reactivity ratios of three P- or P/Br-containing *N*-AMs/St monomer pairs in copolymerization to study their copolymerization behavior. The  $T_g$ s and thermal stabilities of the synthesized copolymers above are also discussed.

## EXPERIMENTAL

### Materials

Styrene (obtained from Tokyo Chemical Industry Co., Ltd.) was distilled under reduced pressure after removal of the inhibitor by the usual method and kept cold before use. Diethyl(*p*-(*N*-phenyl)maleimide)phosphonate(4P), diphenyl(*p*-(*N*-phenyl)maleimide)-phosphonate (PP), and diethyl(*p*-(*N*-(2',6'-dibromophenyl)maleimide)phosphonate) (BrP) were prepared by the method used in our previous paper.<sup>[22]</sup> The synthesized products were dissolved in ethyl acetate and extracted by a 1% NaOH solution. The organic layer was isolated and the remains, dried with anhydrous magnesium sulfate, were then dissolved in ethyl acetate and recrystallized several times with *n*-hexane. The phosphonate-containing MI monomers obtained were dried in vacuum. The characterization of these monomers synthesized was analyzed by the  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared reflection (FTIR) spectroscopy and elemental analysis, respectively.

The initiator, AIBN, was recrystallized from ethanol and dried in a desiccator. Its melting point analyzed by DSC was found to be 104.1°C. Tetrahydrofuran (THF) was distilled after dehydration with sodium. *N,N*-Dimethylformamide (DMF) was dried by  $\text{CaH}_2$  overnight. The other solvents were purified by conventional methods.

### Synthesis of Copolymer<sup>[23]</sup>

A flask was charged with various ratios of St and MI monomers obtained as shown in Table 1, AIBN as an initiator ( $5 \text{ mmole L}^{-1}$ ) and toluene as a solvent. The free radical copolymerization was carried out in a water bath thermostat at 70°C and the mixture was refluxed for a time in which the conversion of copolymerization was restricted to less than 10%. The solvent was removed under reduced pressure, and then the polymerization mixture was again dissolved in dichloromethane and poured into a large amount of methanol. The copolymer was then isolated by filtration and dried under vacuum at 60°C.



## Instrumentation

The IR-spectra and elemental analyses (C, H, N) of the MI–St copolymers were obtained by a Nicolet Omnic 3 FTIR spectroscopy and a Heraeus CHN-O Rapid Analyzer, respectively. The molecular weight distributions of the MI–St copolymers were measured by a Waters Gel Permeation Chromatography (GPC, Waters 1515HPLC/2410RI-detector) at a flow rate of  $1.0 \text{ mL min}^{-1}$  with a sample concentration of 0.5 wt% in THF as effluent flow. The system was first calibrated using standard samples of polystyrene with the narrow distribution of molecular weight. The thermal properties of the synthesized copolymers were investigated by DSC (TA-Instruments DSC 10) at a heating rate of  $10^\circ\text{C min}^{-1}$  in  $\text{N}_2$ , and TGA (TA-Instruments TGA 51) at a heating rate of  $20^\circ\text{C min}^{-1}$  in air or  $\text{N}_2$ , respectively. The flame-retarding properties of copolymers were also studied on a Stanton Redcraft oxygen index analyzer by a modified method: powdered samples (500 mg) were placed in a glass cup (diameter, 25 mm; height, 5 mm) situated in the middle of the chimney and the flame was applied from the top of the chimney for 10 s at an  $\text{O}_2/\text{N}_2$  flow rate of  $20 \text{ L min}^{-1}$ .<sup>[24]</sup>

## RESULTS AND DISCUSSION

### Copolymerization and Copolymer Properties

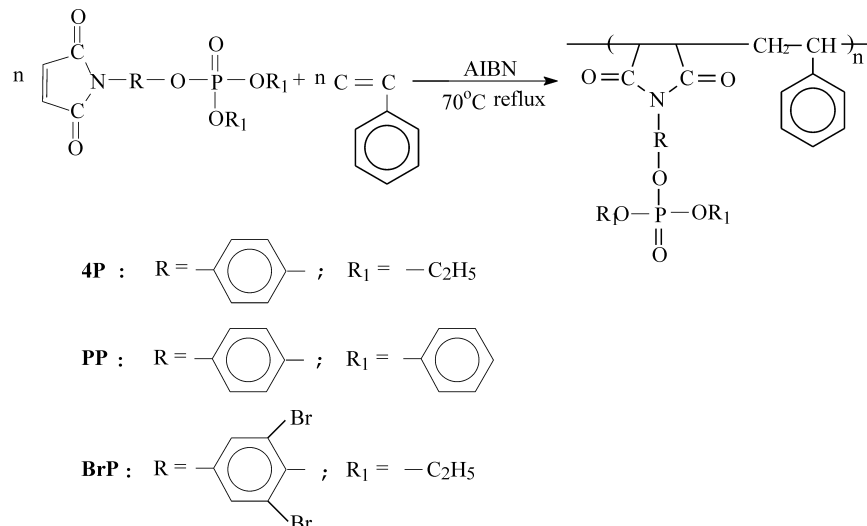
The copolymers of phosphorus-containing *N*-PM with St were synthesized by radical polymerization in a toluene solution using AIBN as an initiator as shown in Sch. 1.

The FTIR spectra of 4P(60%)–St, PP(60%)–St, and BrP(50%)–St copolymers, as shown in Fig. 1, revealed the absorption bands  $\nu$  ( $\text{cm}^{-1}$ ): 1706 (C=O); 1597, 1520 (C=C from benzene); 831 (di-substitution of benzene); 1414 (C–N–C) and 1227–1232 (P=O) from *N*-PM and 700 (mono-substitution of benzene) from St, confirming that all the three series copolymers had been synthesized successfully.

Basic properties of MI–St copolymers in different phosphorus contents and molecular weights obtained from elemental analysis and GPC analysis are given in Table 1. The average number molecular weights ( $\overline{M}_n$ ) of each copolymer series were approximately in the range  $6\text{--}9 \times 10^4$  ( $\text{g mole}^{-1}$ ). The  $\overline{M}_n$  gradually decreased, while the distribution index of molecular weight increased along with the increasing MI monomers in feed. This might be due to the fact that these phosphorus-containing MI monomers could easily cause the chain transfer during their copolymerization reaction. Besides, the copolymerization degree and average molecular weight might be affected by the side-chain effect and steric hinderance generated from MI segments. The sequence of intermolecular steric hinderance should be  $\text{PP} > \text{BrP} > \text{4P}$ . Also, since PP–St series copolymers would form a larger steric hinderance during copolymerization due to PP monomers, a lower polymerization degree and a lower average molecular weight would be obtained.

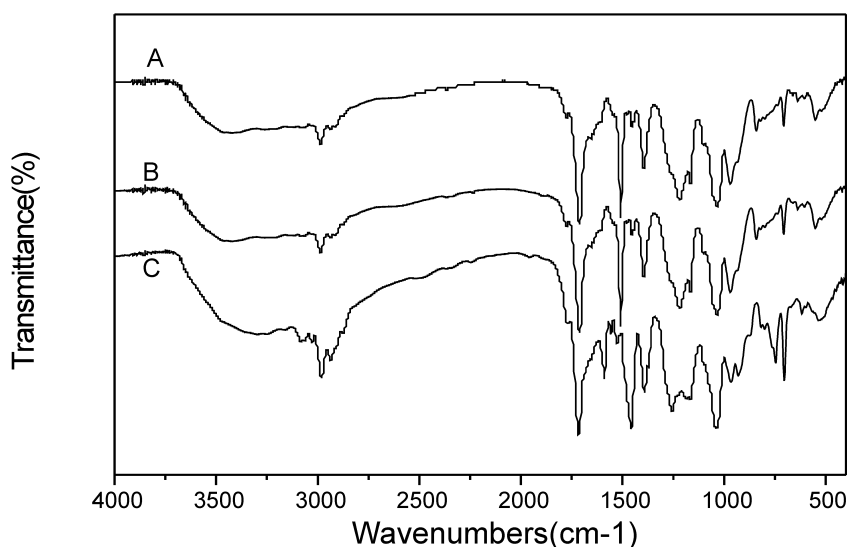
Generally speaking, the double bond of *N*-PM, as a result of the electron-withdrawing effect between carbonyl groups on both sides, showed its reversed polarity vs. St monomers.<sup>[8]</sup> This means the unsaturated double bonds of *N*-PM will be in a state of poor-electron and of St in a relatively rich-electron state. Then, there was a high tendency for those copolymerized to generate alternating-like MI–St copolymers with the reactivity ratios approaching zero. The reactivity ratios of phosphorus-containing MI/St





**Scheme 1.** Synthesis of phosphonate-containing MI-St copolymer.

comonomers, as shown in Table 2, were determined by the method of Mayo-Lewis,<sup>[25]</sup> Fineman-Ross,<sup>[26]</sup> and Kelen-Tüdös<sup>[27]</sup> while the instantaneous copolymer yields were under 10%. All the reactivity ratio for the above copolymerization already produces the change from almost zero to 0.22~0.68, and is larger than that of the general MI-St copolymerization.<sup>[4-8]</sup> This was mainly due to the strong electron-withdrawing effect of phosphonate side chains to inhibit the carbonyl pairs withdrawing electron effect of



**Figure 1.** The FTIR spectra of 4P(60%)–St(A), PP(60%)–St(B), and BrP(50%)–St(C) copolymer.



**Table 1.** Properties of copolymers prepared from phosphorus-containing MI monomers ( $M_1$ ) and St ( $M_2$ ).

Monomer ( $M_1$ )	$F_1^a$ (%)	Conversion	$f_1^a$	$\overline{Mw}^b$	$\overline{Mn}^b (\times 10^4)$	$\overline{Mw}/\overline{Mn} (\times 10^4)$
4P	0.10	9.2	0.16	28.3	9.2	3.08
4P	0.20	9.5	0.25	27.7	8.8	3.15
4P	0.40	8.9	0.42	27.2	8.3	3.28
4P	0.60	7.6	0.56	28.5	8.6	3.31
4P	0.80	8.8	0.69	26.5	7.4	3.58
4P	0.90	8.9	0.80	24.4	6.8	3.59
PP	0.10	8.8	0.18	26.1	8.4	3.11
PP	0.20	8.7	0.26	25.2	8.0	3.15
PP	0.40	9.6	0.43	23.1	7.2	3.21
PP	0.60	9.0	0.57	23.7	6.8	3.48
PP	0.80	9.2	0.68	23.6	6.6	3.58
PP	0.90	9.7	0.79	21.0	5.8	3.62
BrP	0.10	8.6	0.12	25.4	8.9	2.85
BrP	0.20	8.5	0.21	25.9	8.6	3.01
BrP	0.25	9.2	0.26	25.7	8.5	3.02
BrP	0.33	9.1	0.32	25.8	8.1	3.18
BrP	0.50	8.2	0.49	26.0	7.8	3.33
BrP	0.67	8.7	0.64	26.1	7.5	3.48
BrP	0.75	9.3	0.66	25.4	7.1	3.58
BrP	0.80	8.8	0.69	24.6	6.9	3.57

<sup>a</sup> $F_1$  and  $f_1$  are the mole fraction of  $M_1$  in the feed and in the copolymers while  $f_1$  are obtained from element analysis.

<sup>b</sup>Distribution of molecular weight are tested by GPC with a concentration of 0.5 wt.% in THF.

double bond within MI. The result of the reducing reversed polarity of double bond of phosphate-containing MI relative to that of St indicated that the above comonomers reaction is a azeotropic copolymerization, and is similar to the results of the composition ratios of copolymers vs. those of feeds shown in Table 1. As shown in Table 2, the reactivity orders of St-terminated radical towards the 3 series of phosphorus-containing monomers was PP > 4P > BrP, indicating that these copolymerizations were also affected

**Table 2.** Reactivity ratios of phosphorus-containing MI monomers ( $M_1$ ) with St ( $M_2$ ).

Monomer ( $M_1$ )	Mayo–Lewis		Fineman–Ross		Kelen–Tüdös	
	$r_1$	$r_2$	$r_1$	$r_2$	$r_1$	$r_2$
4P	0.28	0.36	0.32	0.46	0.34	0.47
PP	0.22	0.29	0.28	0.34	0.32	0.42
BrP	0.32	0.46	0.38	0.58	0.49	0.61

by the properties of different phosphonate-containing side chains within MI monomers. Since PP monomers had more phenyl rings around phosphorus atoms, the interference caused by phosphorus atoms on the electron-withdrawing effect of carbonyl pairs might be reduced. Therefore, the unsaturated double bonds of PP monomers should have a lower electron cloud density than that of 4P monomers. On the other hand, since the polar bromine and the phosphorus atoms could concurrently offset the electron-withdrawing effect of carbonyl groups, the unsaturated double bonds of BrP monomers should have the highest electron cloud density (BrP > 4P > PP). All the molecular weight, molecular weight distribution or comonomer's reactivity ratios should, therefore, be affected by both steric hinderance and polarity factors of phosphonate-containing side chains simultaneously.

### Thermal Properties of Copolymers

#### Glass Transition Temperature

Glass transition temperature ( $T_g$ ) of copolymers is one of the important physical properties that may be affected by their composition and morphology. All the  $T_g$  data of the 3 series of copolymers are given in Table 3. Since the molecular weights of all the three series of copolymers were higher than  $6 \times 10^4$  (see Table 2), the effect of molecular weight on  $T_g$  was not significant. The DSC measurement for all the copolymers showed that all MI–St copolymers had a single  $T_g$  that would increase along with the increasing MI content. This means that MI and St-segments within the copolymers should be completely compatible. Theoretically,  $T_g$  of the copolymers should comply with the Fox equation<sup>[28]</sup>

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \quad (1)$$

where  $W_i$  was the weight fraction of comonomer  $i$  within the copolymer and  $T_{gi}$  was the homopolymer's  $T_g$  of comonomer  $i$ .

By substituting  $T_{gi}$  into Eq. (1), the real  $T_g$ s of copolymers matching the Fox theory could be obtained. The relationships between the Fox's  $T_g$ -curve and actual  $T_g$ s values, measured by DSC, vs. the copolymer compositions are shown in Figs. 2–4. Considering the segment structures of MI, although their phosphonate-containing side chains were high mobile segments, molecular motions of these segments could only proceed under a relatively higher temperature or energy due to the high rigidity of the imide structure. As shown in Table 3, the  $T_g$ s of all the MI homopolymers and copolymers were higher than that of polystyrene, indicating that the rigid degree of the former was higher than that of the latter. In Fig. 2–4, the actual  $T_g$  curves of copolymers in comparison with the Fox's curves exhibited the positive/negative deviations. The S-like curve of  $T_g$  in the blending polymer system had also been studied in the literature.<sup>[29]</sup> The  $T_g$  of the alternating segments within copolymer ( $T_{g12}$ ) should affect the  $T_g$  of the overall copolymer significantly. Besides, each of the 3 series copolymers had a  $T_g$  value conformed to match the Fox theory (the value at the intersection with Fox's curve), hypothesizing that the comonomer segment-distribution for copolymer in azeotropic composition was more





**Table 3.** Glass transition temperatures of copolymers prepared from phosphorus-containing MI monomers ( $M_1$ ) and St ( $M_2$ ).

Copolymer	$f_1^a$	$W_1^b$	$T_g$ ( $^{\circ}\text{C}$ ) <sup>c</sup>	$T_g$ (K)	$T_{g12}$ (K) <sup>d</sup>
4P–St	0.16	0.3731	130	411	347
	0.25	0.5102	143	418	
	0.42	0.6935	149	425	
	0.56	0.7991	160	431	
	0.69	0.8743	170	437	
	0.80	0.9260	179	445	
	1.00	1.0000	184 <sup>e</sup>	457	
PP–St	0.18	0.4705	135	419	362
	0.26	0.5872	151	429	
	0.43	0.7533	152	431	
	0.57	0.8429	158	432	
	0.68	0.8959	171	437	
	0.79	0.9384	178	447	
	1.00	1.0000	190 <sup>e</sup>	463	
BrP–St	0.12	0.3878	125	404	351
	0.21	0.5525	135	407	
	0.26	0.6200	136	410	
	0.32	0.6861	138	412	
	0.49	0.8169	147	419	
	0.64	0.8920	156	429	
	0.66	0.9002	162	431	
	0.69	0.9118	167	433	
	1.00	1.0000	174 <sup>e</sup>	447	

<sup>a</sup>Mole fraction of  $M_1$  within the copolymer.<sup>b</sup>Weight fraction of  $M_1$  within the copolymer.<sup>c</sup>The glass transition temperature ( $T_g$ ) is analyzed by DSC at a heating rate of  $10^{\circ}\text{C min}^{-1}$  in  $\text{N}_2$ .<sup>d</sup>Glass transition temperature calculated by the modified equation of Johnston.<sup>e</sup>The data of homopolymer were used from the previous study (Ref.<sup>[22]</sup>).

random than that in the others, leading to offset the alternate segment effect. On the other hand, except for the copolymer with azeotropic composition, the molecular motion of the others was easily affected by its alternate segment. Therefore, a higher content of phosphonate-containing MI segment within copolymer would produce a negative deviation of  $T_g$  due to the effect of St segment, and on the contrary, a lower content would produce a positive deviation of  $T_g$  due to the effect of MI segment. In order to understand the effect of the alternate segment for the actual  $T_g$ s of copolymers, the Johnston's equation<sup>[30]</sup> modified from Fox theory was applied:

$$\frac{1}{T_g} = \frac{W_1 P_{11}}{T_{g11}} + \frac{W_2 P_{22}}{T_{g22}} + \frac{W_1 P_{12} + W_2 P_{21}}{T_{g12}} \quad (2)$$



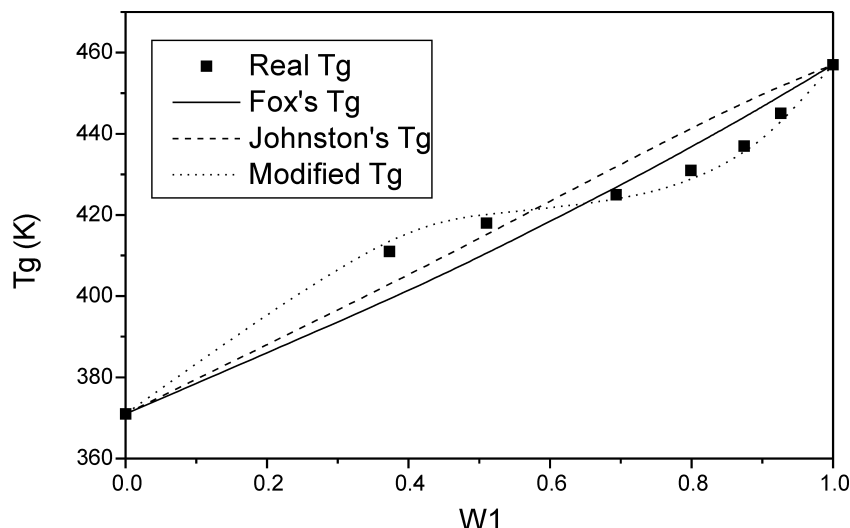


Figure 2. Variation of  $T_g$  as a function of the weight fraction of diethyl(*p*-(*N*-phenyl)maleimide)-phosphonate ( $W_1$ ) for the 4P-St copolymer system.

where  $P_{ij}$ : probability of forming  $ij$ -segment,  $T_{gii}$ : homopolymer's  $T_g$  of comonomer  $i$ , and  $T_{gij}$ : glass transition temperature of alternating segment within copolymer. The  $P_{ij}$  could be calculated as:

$$P_{12} = \frac{1}{1 + r_1([1]/[2])} = \frac{1}{1 + r_1(f_1/f_2)}$$

$$P_{21} = \frac{1}{1 + r_2([2]/[1])} = \frac{1}{1 + r_2(f_2/f_1)}$$

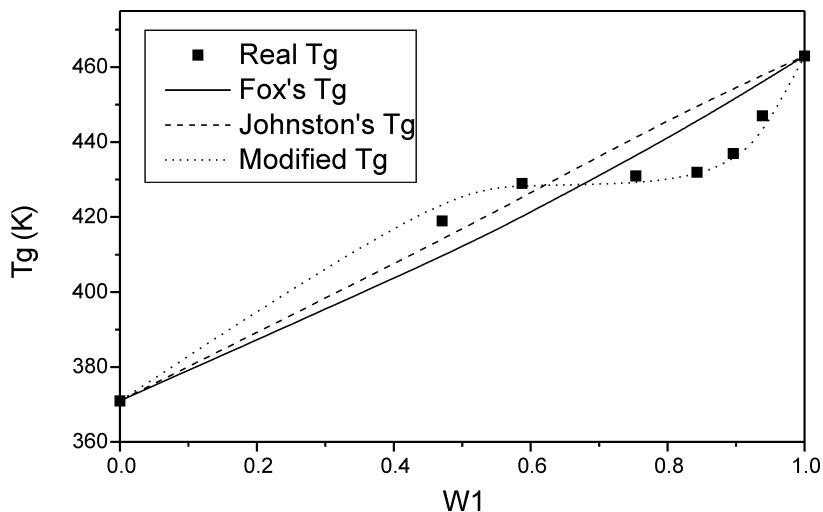
$$P_{11} = 1 - P_{12} \quad P_{22} = 1 - P_{21}$$

It could also be noticed in Figs. 2–4 that the Johnston's curves of copolymers did not match the actual  $T_g$  curves. This means the effect of its  $T_{g12}$  on the real  $T_g$  of copolymer cannot be sufficiently described by Johnston's equation. Considering the influence of  $T_{g12}$  that should be more significant, a modified Johnston's equation can be taken as following:

$$\frac{1}{T_g} = \frac{W_1 P_{11}}{T_{g11}} + \frac{W_2 P_{22}}{T_{g22}} + \frac{W_1^\alpha P_{12} + W_2^\alpha P_{21}}{T_{g12}} \quad (3)$$

where  $\alpha$  is a parameter according to the effect of alternating segment. Substitution of actual  $T_g$  of all the 3 series copolymers into the Eq. (3) gave an average of  $T_{g12}$  so as to obtain the modified  $T_g$ - $W_1$  curves. It could also be noticed from Figs. 2–4 that the actual  $T_g$  of all the 3 series of copolymers were proved to match our modified curves while  $\alpha = 1.40$  in 4P and PP series and  $\alpha = 1.37$  in BrP series. That means the  $T_g$  of these copolymers could be sufficiently described by our modified equation as a result of increasing the affect of weight ratio on  $T_{g12}$ .

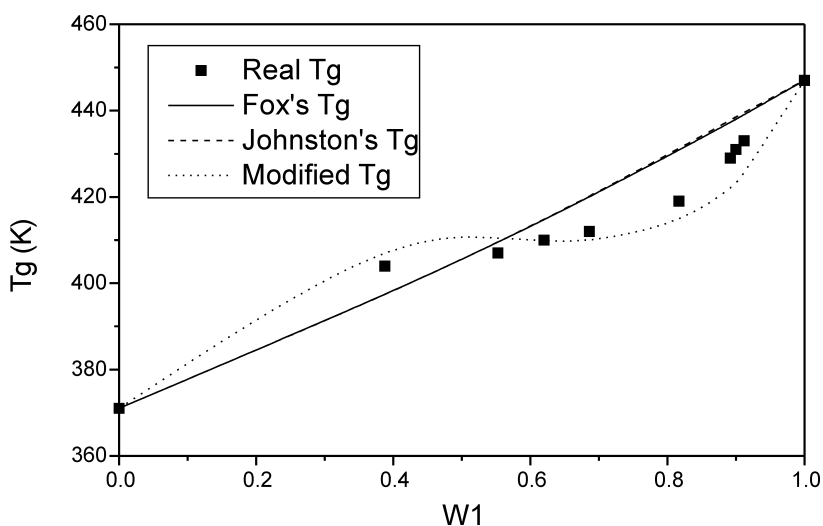




**Figure 3.** Variation of  $T_g$  as a function of the weight fraction of diphenyl(*p*-(*N*-phenyl)maleimide) phosphonate ( $W_1$ ) for the PP-St copolymer system.

### Thermal Stability

The thermal properties of three series MI-St copolymers analyzed by TGA in nitrogen and in air at a heating rate of  $20^\circ\text{C min}^{-1}$  are shown in Figs. 5–10. The temperatures of 5% wt. loss ( $T_{5\%}$ ) and char yields of solid residues at  $800^\circ\text{C}$  are given in Table 4. As compared to the  $T_{5\%}$  in Table 4, the thermal stability of each copolymer series was lower than that of pure polystyrene. However, the phosphonate-containing side chains with high rigidity (e.g.



**Figure 4.** Variation of  $T_g$  as a function of the weight fraction of diethyl(*p*-(*N*-(2',6'-dibromophenyl) maleimide)phosphonate) ( $W_1$ ) for the BrP-St copolymer system.



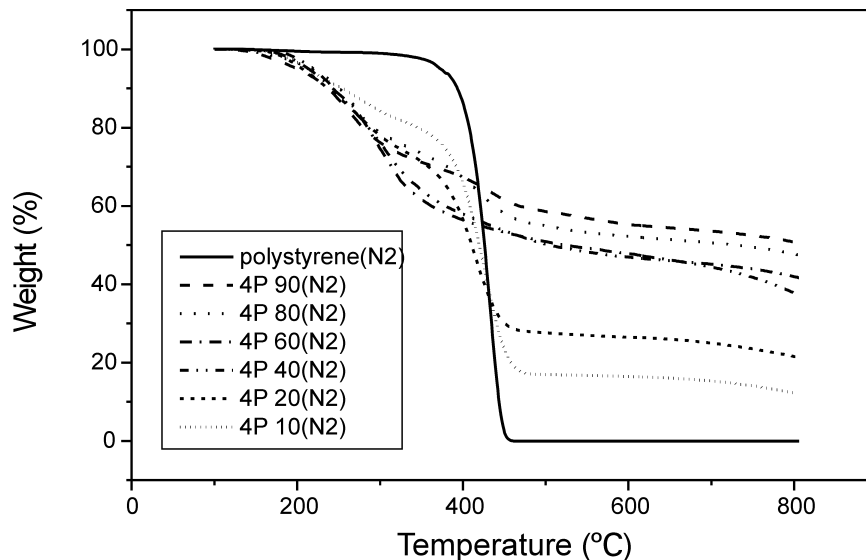


Figure 5. TGA traces of 4P-St copolymers in N<sub>2</sub>.

PP-St series) or bromine atoms with relatively high polarity (e.g. BrP-St series) within the MI segment could increase thermal stability of copolymers in nitrogen or in air. An increase in thermal stability, particularly for PP-St and BrP-St series, was even more significant in oxidation environment. Hence, it was obvious that high rigidity groups or high polarity bromine atoms could increase the anti-oxidation ability of copolymers. Also,

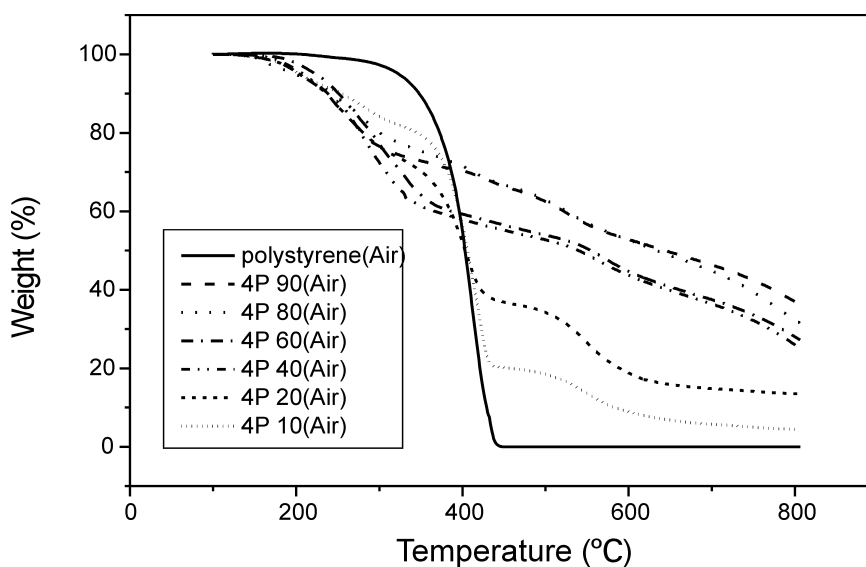


Figure 6. TGA traces of 4P-St copolymers in air.



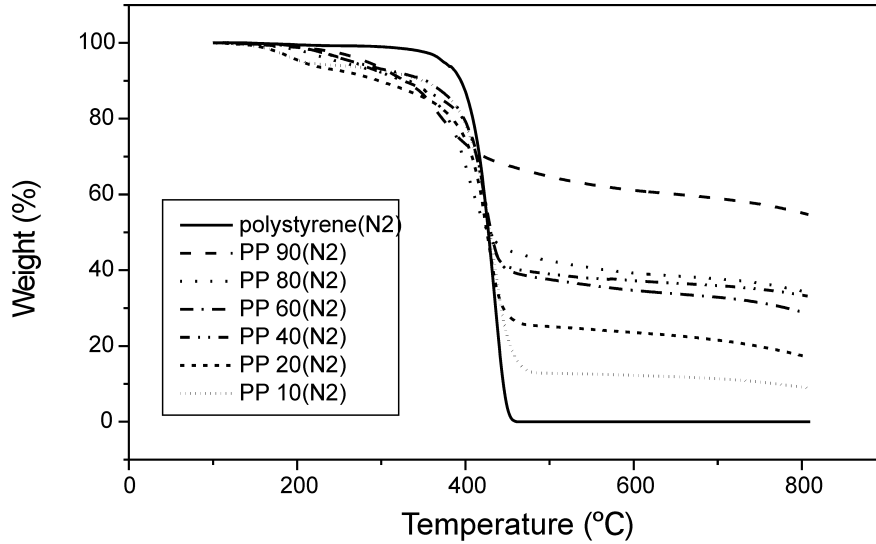


Figure 7. TGA traces of PP-St copolymers in N<sub>2</sub>.

as mentioned before, the segments distribution of the MI-St copolymers near the azeotropic composition tended to be more random, indicating that the synergy effect of the above comonomer-segments could promote simultaneously the thermal stability and flame retardancy.

The TGA traces of 4P-St copolymers measured in nitrogen and air are shown in Figs. 5 and 6, respectively. The scission of the copolymers with 40–60 mol% of 4P content in

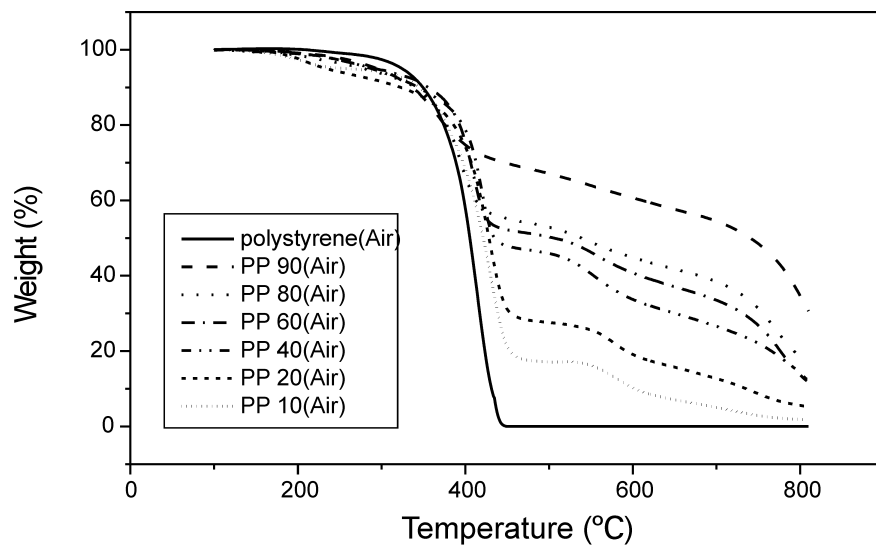


Figure 8. TGA traces of PP-St copolymers in air.



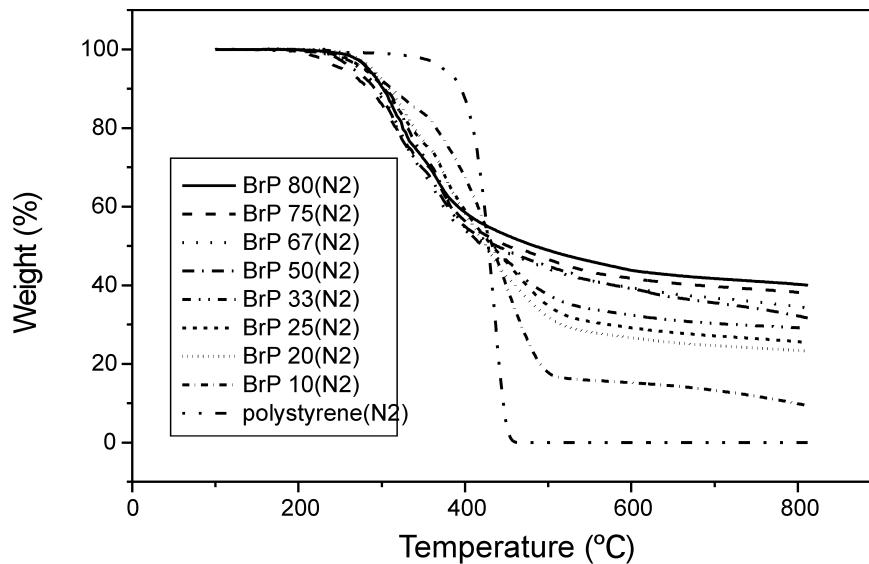


Figure 9. TGA traces of BrP-St copolymers in N<sub>2</sub>.

nitrogen and air was a one-stage and a two-stage process, respectively. But the scission of the copolymer with other 4P content in nitrogen and in air was a two-stage and a three-stage process, respectively. This also exhibited the synergy effect of 4P-St segments at about 40~60 mol% 4P contents of copolymers nearby the azeotropic composition. The scission of phosphonate side chains of copolymer should first be initialized and then, its

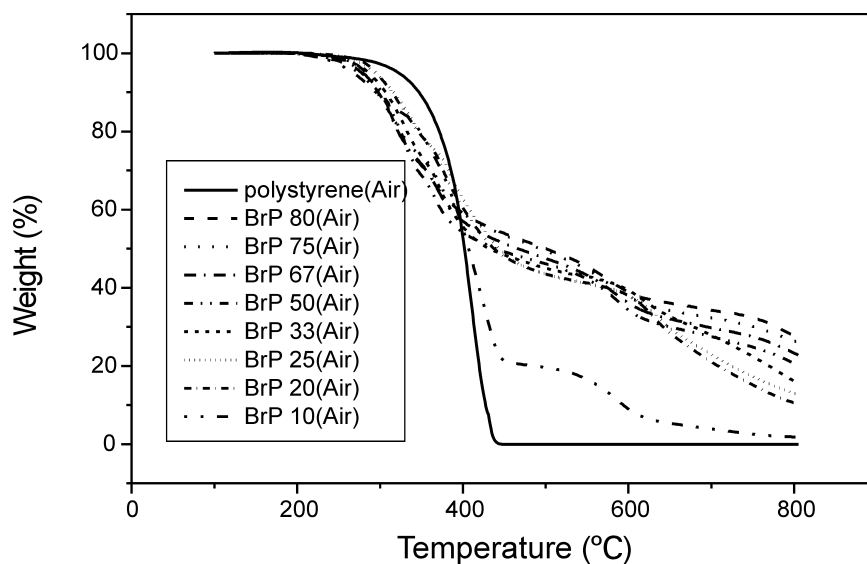


Figure 10. TGA traces of BrP-St copolymers in air.



**Table 4.** Thermal properties of copolymers prepared from phosphorus-containing MI monomers ( $M_1$ ) and St ( $M_2$ ).

Monomer ( $M_1$ )	$F_1^a$	$f_1^b$	$P$ (%) <sup>c</sup>	5%wt. Loss (°C) <sup>d</sup>		Char at 800°C (%) <sup>d</sup>		LOI
				Air	N <sub>2</sub>	Air	N <sub>2</sub>	
4P	0.10	0.16	3.56	204	207	4.4	12.2	20
	0.20	0.25	4.87	205	213	13.5	21.6	26
	0.40	0.42	6.62	218	220	26.0	37.8	36
	0.60	0.56	7.62	223	217	28.1	41.9	41
	0.80	0.69	8.34	204	214	32.4	47.7	45
	0.90	0.80	8.83	200	200	37.0	50.7	48
	1.00	1.00	9.54	232	256	40.1	55.2	51
PP	0.10	0.18	3.46	234	206	1.9	9.2	19
	0.20	0.26	4.32	255	207	5.6	17.5	23
	0.40	0.43	5.55	288	267	14.3	29.0	30
	0.60	0.57	6.21	292	266	13.9	33.5	33
	0.80	0.68	6.60	288	270	18.5	34.6	35
	0.90	0.79	6.91	295	283	35.0	55.2	47
	1.00	1.00	7.36	325	328	41.2	45.2	49
BrP	0.10	0.12	2.49	277	280	1.8	9.9	26
	0.20	0.21	3.55	295	288	10.7	23.4	29
	0.25	0.26	3.98	294	285	13.0	25.7	32
	0.33	0.32	4.40	286	286	16.2	29.2	34
	0.50	0.49	5.24	284	274	20.7	32.3	38
	0.67	0.64	5.72	279	266	23.4	34.6	40
	0.70	0.66	5.78	274	263	26.5	38.2	41
	0.80	0.69	5.85	277	284	27.8	40.2	41
	1.00	1.00	6.42	266	270	30.6	30.1	44
PS <sup>e</sup>	—	—	0.00	323	373	0.0	0.0	18

<sup>a</sup>Mole fraction of  $M_1$  in the feed.

<sup>b</sup>Mole fraction of  $M_1$  within the copolymer.

<sup>c</sup>The theoretical calculation values of  $P$  composition ratio.

<sup>d</sup>Thermal properties is analyzed by TGA at a heating rate of 20°C min<sup>-1</sup> in N<sub>2</sub> or in air.

<sup>e</sup>Polystyrene with a Mn about  $1.5 \times 10^5$ .

main chains of MI and St segments were again decomposed either at the same stage or at different stage. For an oxidation environment, its unstable carbonized solid residues after the decomposition of main chains within copolymer could be thermally oxidized gradually at the last stage. Therefore, as the composition of copolymer is similar to the azeotropic composition, their decomposition process for the first stage in air was still initialized by its phosphonate side chain and then the main chain. For the second stage, their solid residues were again thermally oxidized. For other copolymers compositions, the scission of phosphonate side chain and main chain in air occurred at the first and the second stages, respectively, then, the oxidation at the third stage. The TGA traces of PP–St copolymers in nitrogen and in air are shown in Figs. 7 and 8, respectively. The decomposition for all the



PP–St series copolymers in nitrogen and in air was a one-stage and two-stage process, respectively. The high phenyl density of PP–St copolymers results in the higher thermal stability. The TGA traces of BrP–St copolymers are shown in Figs. 9–10. In a nitrogen and air environment, only the BrP–St copolymer with 10 mol% of MI content showed a two- and three-stage process, respectively. The BrP–St copolymers with other MI content showed a one- and two-stage process, respectively. This might be due to the fact that comonomer compositions of the BrP–St series copolymer above 20 mol% BrP content could increase their synergy effect so as to promote the thermal stability.

The phosphorus content always affected the char yield of organic materials at high temperature significantly. Generally, the increase of phosphorous content within copolymer increased its char yield of solid residues during thermal decomposition due to the occurrence of chain transfer forming the P–C glass phase. For the three series of copolymers in the same comonomer mole ratios, the orders of phosphorus content were 4P-series > PP-series > BrP-series. It was known from Table 4 that, in nitrogen or in air, the increase of MI content within all three series copolymers increased their pyrolyzed char yield of solid residue at 800°C. When there was a higher ratio of St-segment in copolymer, the char yield per unit phosphorus content was apparently lower. So, when the MI content of 4P-series, PP-series, and BrP-series copolymers were less than 4P-20, PP-20, and BrP-20 mol%, respectively, their pyrolyzed char yield via flame resistance would apparently be lower than other compositions of the same series. Then, the pyrolyzed char yield of solid residue on PP–St copolymer about PP-90 mol% content in nitrogen at 800°C was higher than that of the PP-homopolymer, indicating that the synergy effect of the PP- and St-segment on copolymer could promote its flame resistance. For a BrP content more than 33 mol% in BrP–St series, their pyrolyzed char yield in nitrogen at 800°C was higher than that of the BrP-homopolymer. This could be explained that there was not only a synergic fire resistance effect from BrP- and St-segment from polarized bromine atom and phosphorus atom within BrP-segment. Therefore, the BrP–St copolymers showed a higher fire retardant effect even at a low BrP content. In Table 4, for example, the char yields of 4P-90, PP-90, and BrP-90 mol% copolymers pyrolyzed in nitrogen were 50.7, 55.2, and 40.2%, respectively. The latter two were over 25% higher than that of PP and BrP homopolymers, respectively. The flame resistance of all the 3 series of copolymers could also be confirmed by the results of fire retardancy test (as given in Table 4). Generally, the LOI values increased with increasing the phosphorous content within copolymers. Since there was a synergic fire resistance effect from BrP- and St-segment from polarized bromine atom and phosphorus atom within BrP-segment, the copolymers of BrP series also showed a higher LOI.

## CONCLUSION

The radical copolymerizations of three-series phosphonate-containing MI with St were carried out to get the azeotropic copolymers. The factors, such as steric hinderance and polarity caused by phosphonate-containing MI, could affect the molecular weight, distribution index and segments distribution of copolymer. The actual  $T_g$ s curves vs. the composition ratios for all the above copolymers were very consistent with the modified Johnston's equation as increasing the weight ratio of alternate segments. Besides, the thermal stability and flame retardancy of the copolymer were also affected by its segment-distributions, side chain structures, and compositions. The more the rigidity of







phosphonate-containing MI within the copolymer, the higher its thermal stability and flame retardancy. The azeotropic composition, phosphorus content, and P/Br synergy effect of the above copolymer further affect the thermal stability and flame retardancy. The synthesized phosphonate-containing MI copolymer systems should be a series of excellent flame retardant in electric materials application due to their high  $T_g$ , good thermal stability and flame retardancy.

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